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Program Manager: Originally, Major Jennifer Gresham (Chemistry & Life Science). Replaced by Major Michelle E. Ewy (Rauch), Ph.D.

Contract/Grant Title: "Organically doped metals: A new family of materials"

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1. Overview

As detailed below, we have made major progress in a number of directions in further developing applications of the new materials technology, which enables us to incorporate and entrap small organic molecules, polymers, biomolecules, and nanoparticles within metals. This general materials methodology has been unknown: the first publication [1] did not cite prior art; thus it comprises an original advanced general materials methodology. These developments have already attracted a great deal of attention, represented, for instance, by highlights in *C&EN* [14] and in *Angew. Chem.* [13], and by the selection of ref. 8 as one of the most interesting 2008 chemistry papers [12]. Here are the details:

2. Motivation

Let us first recall the motivation for this project: There are more than 24 million known organic and bioorganic molecules, which represent a very rich library of chemical, biological, and physical properties that the ~100 metals are devoid of. One can imagine the huge potential which can be opened by the ability to tailor metals with any of the properties of organic molecules. Metals will then have not only the traditional properties and applications, but also many new properties, which will merge their classical virtues (e.g., conductivity and catalytic activity) with the diverse properties of organic molecules. Likewise one expects that the incorporation of an organic or bioorganic molecule within the sea of electrons of a metal will affect its properties, inducing new reactivities - catalytic or otherwise - of these dopants, and modifying their physical properties. As we have indeed found, one might expect that the creation of dopant@metal (we use this notation for these hybrids) will yield new properties which are more, or different than the sum of the individual properties of the two components, namely that synergism will emerge in these hybrid materials [1-11].

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14. ABSTRACT Organically doped metals have been the focus of this program. Diverse directions of research have been employed, leading to a wealth of results and new insights have resulted. These include: 1. The development of an electrochemical entrapment method. 2. The development of an entrapment method tailored to hydrophobic polymers. 3. The development of several novel catalysts, notably the new concept of an organometallic catalyst entrapped within a metal. 4. The development of a methodology for entrapment of enzymes within silver and gold. 5. The demonstrating of the ability to control metal conductivity through polymers doping. 6. The induction of chirality within Ag, Au and Pd, and the use of the latter for enantioselective catalysis.					
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3. Background

Attempts to merge these two worlds (in the materials sense; not in the molecular sense where organometallic compounds are of course well known) have so far been confined to separation of manufacturing steps and of the location of the metal and organic molecules. Thus, metals and organic molecules have appeared as distinct domains in the same context in various ways, such as adsorption onto metal surfaces, polymeric coatings of metals, dispersion of (colloidal) metals in bulk polymers, thin films or particles, and surface metallization of polymeric surfaces [15-20]. Our goal and vision have been different: We aimed at incorporating an organic molecule *within* a metallic matrix. As mentioned above, we have not encountered earlier reports on directed efforts to create organically doped metals as a new family of functional materials. Studies which border it in some way are some propositions that metal electrodeposition in organic media may result in organic impurities [21], Warshawski's et al studies of the surface metallization of polymer microbeads with added or tethered dyes [20], and the high-temperature co-sublimation of magnesium and rubrene [22].

The basic approach we have been developing is the reduction, at room temperature, of a metal cation, in the presence of the desired dopant (Fig. 1). Conditions have to be created such that the precipitating metal will capture the dopant, while it forms. Different synthetic methods have been developed (and are still being developed as part of this proposal- see below), in which the reducing agent is either water soluble [1], or DMF for water insoluble polymers [8], or a metallic powder, which is above the reduced cation in the electrochemical series [4], or an electric current (still under investigation). The relative amount of the organic component can vary (depending on the system parameters) between less than 1 molar% (doping in the true sense of the word) and several ten of % (true hybrid; for simplicity we use the terms "doping" and "hybrid" for all percentages). A large battery of analytical tools has been employed to gain an insight on the structure of these new materials. The picture that has emerged is of entrapment within the agglomerated nanocrystals (Fig. 2), to such an extent that water-soluble entrapped molecules, cannot be extracted by water. An important and very useful property of the porosity, is that the dopant is accessible for chemical reactions; this has been utilized for catalysis – see below. Entrapment and adsorption are very different processes in this context. Thus, the same molecules are easily washed away if only adsorbed. Most of the special properties we that we have observed to date – such as major improvements or changes in catalytic activity, completely different TGA behavior, and more – are observed in the entrapped cases, but not in the adsorbed ones.

Homogeneous entrapment in silver

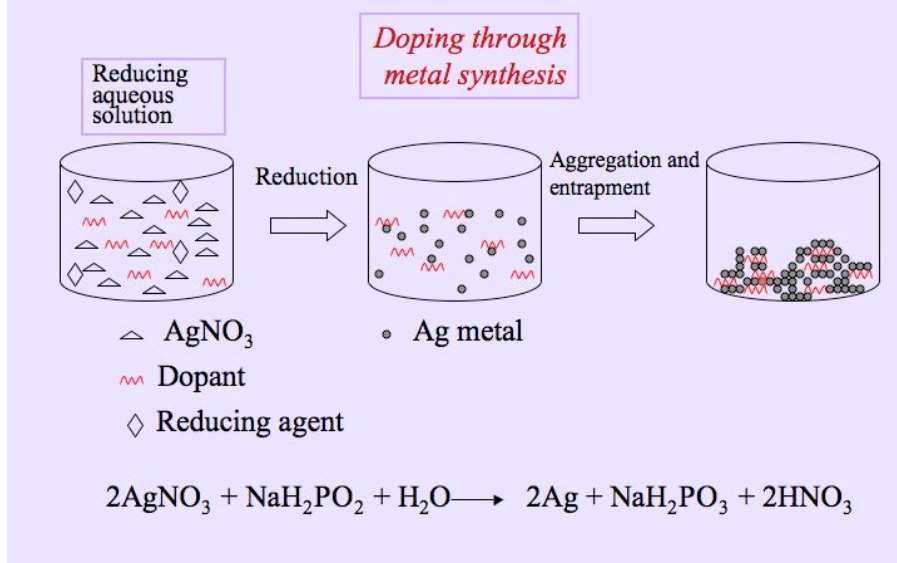


Fig. 1: The entrapment of an organic dopant within a metal is carried out by the reduction of the metal cation in the presence of the molecules to be entrapped. By careful selection of the reducing agent and the reaction condition, a dopant@metal hybrid material, results, as powders which can be pressed to coins.

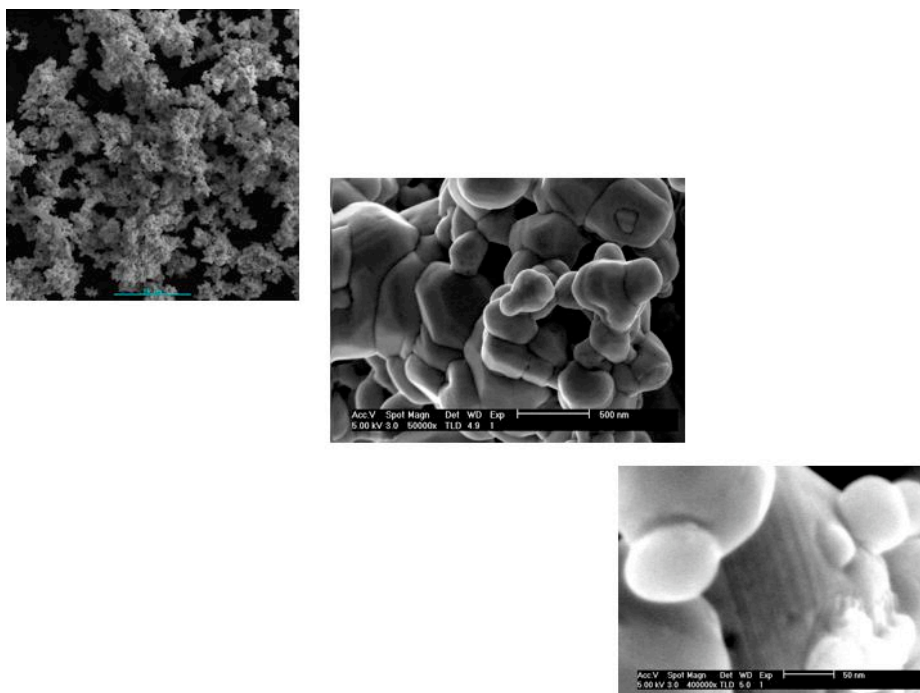


Fig. 2: The hierarchical structure of the hybrid materials. Shown is the hybrid between poly(styrene sulphonic acid) and silver. Left: The porous structure on a microns scale (bar: 16 microns). Middle, the aggregated crystals (bar: 500 nm). Right: Oozing out of the entrapped polymer caused by the electron energy (bar: 50 nm). XRD provided another scale, showing that the elementary crystallites are on the ~20 nm scale.

4. The research achievements

4.1 Development of new entrapment methodologies:

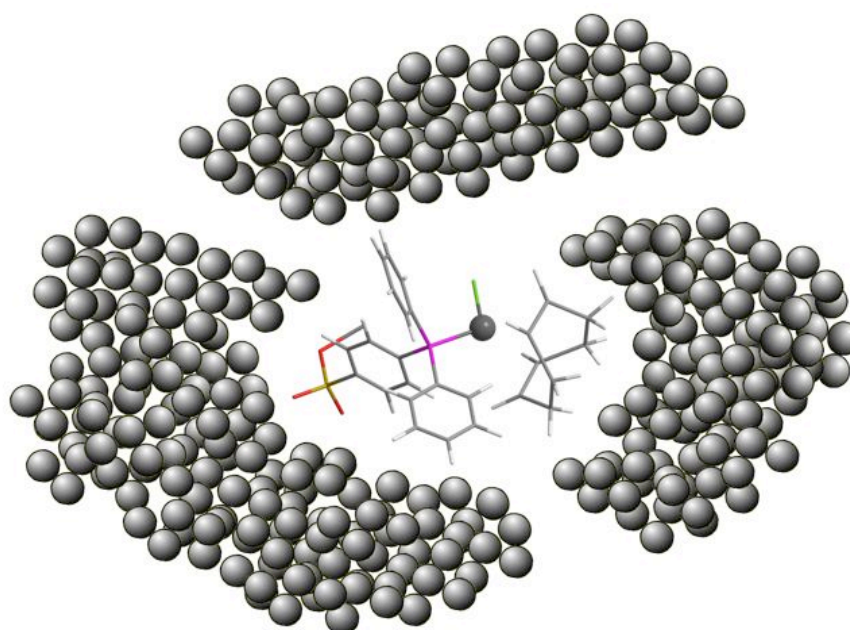
I. The main entrapment methodologies which have been in use so far include homogeneous reduction of metallic cations with either small-molecules reducing agents or with metal powders (such as Zn). A major aim of this proposal was to enrich the arsenal of synthetic methods and materials architectures of these hybrid materials, and in particular electrolytic entrapment. This has been achieved [11b]: An electrolytical method was developed for the doping of metal with organic molecules (0.1-1% by weight). Several representative organic molecules, including dyes and polymers, have been entrapped in copper or silver using this procedure. The resulting doped metals have been fully characterized using TGA, UV-Vis, SEM, EDS and XRD. The dynamics of dye extraction from composites has been modeled, offering a means to quantify the leaching behavior of organics@metals. Typically, entrapped molecules are shown to be heterogeneously distributed within the composites, including a population which is entrapped tighter than with non-electrolytic methods.

II. A second challenge we have solved [8] is the entrapment of water-insoluble hydrophobic polymers in a metallic matrix, thus generalizing further the routes for obtaining the novel organics@metal composite materials. The reaction took place in an organic phase using the reduction of metal ions by DMF in the presence of water. The reductive entrapment of polyaniline was studied in detail using XRD, SEM, BET, TGA, UV-vis, XPS, and density measurements, and the mechanism of the entrapment was established. The scope of this approach was demonstrated by entrapment of two additional hydrophobic polymers polystyrene and polyacrylonitrile.

4.2 Doped metals - a new concept for heterogeneous catalysis: The fact that the dopant within the metal is accessible for external molecules diffusing into it, and the mesoporosity of these materials, open the possibility to do interesting chemistry with these hybrids, and in particular catalysis. Indeed, as metals play a key role as catalytic materials, one of the main foci of this program has been the investigation of the performance of doped metals as new catalysts - what are the new aspects they can contribute to this central field of chemistry? Which dopants are relevant for altering the activity of the metal? Can synergism between the metal and the dopant be observed? We propose to explore these questions in three different directions, based on the feasibility stage carried out on Ag. In the first of these directions we were able to render silver either acidic or basic by the entrapment of a suitable polymer. For instance, when the polyacid Nafion was successfully entrapped, "acidic" silver resulted (this is of course an unorthodox property of this metal). Nafion@Ag was then tested as a heterogeneous acidic catalyst for the pinacol-pinacolone rearrangement, and was found very efficient [3]. With this we have demonstrated for the first time that a metal can serve as a support for homogeneous catalysts. We are also aiming here at another concept we wish to test, that is, bi-functional catalytic materials, in which both the dopant and the metal will act as different catalysts for consecutive reaction steps (in this example, Nafion as an acidic catalyst and Ag is an oxidation catalyst).

The second direction focuses on the metal itself - can its catalytic properties be affected by the dopant? Again, very encouraging results were obtained for Ag [6]: Doping of Ag with Congo Red (CR@Ag) following by thermal activation of the hybrid material, significantly improves the performance of Ag as a catalyst for methanol oxidation to formaldehyde (a high industrial volume process), outperforming both pure Ag and CR-coated Ag in terms of lowering the temperature needed for maximal conversion by 100 °C. The third direction, perhaps the most exciting one, has been demonstrated in 2008 [7], and indeed has already attracted significant attention [12-14], as detailed in Section 1 (Background). The new concept that was proposed is the entrapment of an organometallic catalytic complex within a catalytic metal. The feasibility of this idea was proven with $(\text{RhCl}(\text{COD})(\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{Na})))$, $([\text{Rh}])$, entrapped within silver, $([\text{Rh}]@\text{Ag}$, Fig. 3). Several aspects were demonstrated with the development of this heterogeneous catalyst: again, that a metal can be used as a support for heterogenizing a homogeneous catalyst; that the homogeneous catalyst is stabilized by the entrapment within the metal; that the products of the composite catalyst are different compared to those obtained from the homogeneous one; and that adsorption of $[\text{Rh}]$ on the surface of Ag and its entrapment are very different processes - only the latter provided appreciable catalytic activity.

Overall, as metals are so central in catalysis, we envisage that one of the main impacts of this project will be in this field: merging organics into metals is a powerful way to fine-tune the catalytic properties of metals.



Rhodium phosphine cyclooctadiene complex entrapped within a matrix of silver particles forms a synergistic catalytic system

Fig. 3: Schematic illustration of the new heterogeneous catalysts: A catalytic organometallic complex entrapped within a metal. The metal can be either an inert matrix, or a catalytic metal. In the latter case, interesting synergism may emerge.

4.3 Entrapment of enzymes within metals. A natural extension of the catalysis sub-program is biocatalysis, namely to obtain enzyme@metal hybrids. The intensive activity in the development of enzyme-immobilization methodologies has focused mainly on organic polymers [23,24], on metal-oxide matrices such as sol-gel materials [25-28] and on their composites [29]. In principle, the third major immobilization-material option is provided by metals, and here the main activity was the association of enzymes with metallic interfaces or thin films [32,33]. Here too we have a proof of feasibility at hand and a clear demonstration that entrapping leads to a distinctly different bioactive material, compared to adsorption. Thus, we have been able to immobilize successfully two enzymes, acid phosphatase and alkaline phosphatase [9] in either silver or gold. The entrapped enzymes retained their catalytic activities in the resulting metal powder and kinetic investigation revealed Michaelis-Menten behavior. Protectability of the entrapped enzyme against harsh conditions was shown: The acidic enzyme was kept alive under basic conditions. Adsorption of the enzymes on these metals afforded significantly inferior activity.

4.4 Biocidal doped silver. The second bioactive system developed was a biocidal composite that incorporates a variety of biocidal agents (antibacterial, antibiotic, antifungal and antiviral) in silver, a metal well known for its own biocidal activity. Preliminary antibacterial investigations of these new biocidal composites showed enhanced activity against wild-type *E. coli* in comparison to their individual components. Biocidal activity tests of (chlorhexidine digluconate)@Ag revealed high *synergistic* activity of the sustainable release of its components, namely chlorhexidine molecules and Ag^+ . A very encouraging observation has been demonstrated on a *E. coli* strain, which is insensitive to silver on a 24 hrs time scale, demonstrating also the potential use of this product for hospital Ag-resistant bacteria (~1/3 of hospital strains).

4.5 Affecting conductivity. Conductivity is perhaps the immediate classical physical property of metals that come to mind, that are expected to be affected, even tailored, by the use of selected dopants. We have focused on polyaniline@Ag for that purpose, and indeed found [10] that the polymer concentration and its MW influenced this material property. Pressed films were utilized to measure the electrical conductivity of the composites in order to study the polymer-silver interactions at the molecular level and to establish a correlation between the microscopic morphology and the film conduction. Such correlations have been identified, and were interpreted.

4.6 Chirality of metals. We were seeking to develop metals with a property which is usually not associated with these materials - chirality. Chirality has been a central research theme in our group, both theoretically [36] and experimentally [37]. It was therefore natural for this group to try and induce chirality in metals by the doping methodology. It worked: We provided evidence of induction of chirality in gold and silver doped with L-glutathione or L-quinine or either D- or L- tryptophan. Thus, clear differences in the emission efficiency of photoelectrons (see ref.'s 38 and 39 for the experimental setup) were observed, when discs of these composite materials were irradiated with either clockwise or anti-clockwise circularly polarized UV light [5].

Finally, an on-going challenge is to form enantioselective metal catalysts, not by using an adsorbed chiral modifier as is currently done [40,41], but by using a *chirally imprinted metal* (Pt and Pd). We recall that chiral catalysis is highly needed for the synthesis of pharmaceutical intermediates. A first step in that direction has been achieved and was published recently in *Nature-Chemistry* [11a]. Specifically, a Pd coin doped with 1% cinchonidine alkaloid was shown to catalyse the hydrogenation of isophorone with molecular H₂, giving an average of 16% ee in triplicate experiments. The surface properties of the metal-organic composites were characterized with high-resolution scanning electron microscopy, X-ray diffraction and nitrogen adsorption techniques, showing a porous microscopic structure. The chirality was proved using electron photoemission spectroscopy and *in situ* adsorption and extraction kinetics using UV-visible spectroscopy. Excitingly, the latter two prove that the Pd metal retains its chiral properties even after the dopant is removed; the alkaloid modifier is necessary, in this case, for obtaining enantioselective catalysis.

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